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EXPERIMENT

Ni(II) Schiff Base Complexes: An Introduction to Diamagnetism and Paramagnetism Using Benchtop NMR Spectroscopy



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INTRODUCTION

Historically, the technique of NMR has mostly been restricted to the study of organic molecules.¹ However, a lot of research has been performed on NMR of paramagnetic species, which can include radical-containing molecules or many transition metal complexes.² Many important catalytic processes are made possible via the intermediacy of transition metal complexes in exotic oxidation states, which can lead to unique geometries and ultimately unpaired electrons.³ While NMR remains one of the most powerful tools for chemists with regards to structural elucidation, the presence of unpaired spins can make this process much more difficult. Extreme and difficult to predict chemical shifts, very broad signals with low signal-to-noise, and loss of coupling information all contribute to complex spectra.⁴

Despite the disadvantages inherent to paramagnetic NMR, chemists have characterized a wide array of paramagnetic complexes and this technique continues to prove itself as a

crucial characterization tool across all areas of chemistry.² While undergraduate students are often introduced to the concept of paramagnetism in the classroom, this theory rarely extends to the laboratory. This is unfortunate, as it can serve as an important tool for teaching concepts such as coordination geometry, d-orbital splitting, magnetic susceptibility, the effect of unpaired electrons on NMR spectra, and many others.

In this Application Note, two Ni(II) Schiff base complexes are prepared and their very different NMR spectra are compared and analyzed, based on work published by Venable in *The Journal of Chemical Education*.⁵ One of the complexes is diamagnetic and affords what might be deemed a 'normal' NMR spectrum, while the other complex is paramagnetic and gives rise to a very different type of spectrum. The effect of functional group size on geometry is explored, and important teaching concepts are touched upon.

EXPERIMENTAL

Materials

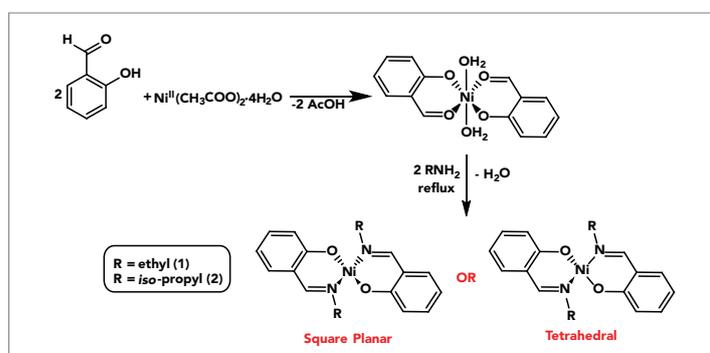
Salicylaldehyde ($\geq 98\%$), nickel(II) acetate tetrahydrate (98%), ethylamine (66.0%-72.0% in H_2O), amine ($\geq 99.5\%$), and chloroform- d (99.8%) were purchased from MilliporeSigma and used without further purification.

Instrumentation

All NMR data was obtained at 32 °C using a 60PRO instrument at 60.73 MHz proton frequency. The ^1H experiments were performed using the following parameters: spectral width, 20 ppm for complex **1** (230 ppm for complex **2**); spectral center, 5 ppm for complex **1** (100 ppm for complex **2**); number of points, 8192; scans, 64 for complex **1** (256 for complex **2**); dummy scans, 0; interscan delay, 1 second; pulse angle, 80.77°. The ^{13}C experiments were performed using the following parameters: spectral width, 220 ppm; spectral center, 100 ppm; number of points, 4096; scans, 16384; dummy scans, 0; interscan delay, 0 seconds; pulse angle, 62°. All chemical shifts were reported in parts per million (ppm) relative to CDCl_3 , referenced at 7.26 ppm for ^1H and 77.16 ppm for ^{13}C . All spectra were manually corrected for phase and baseline distortions using MestReNova software (v14.1.1).

Synthesis

The synthesis of two Ni(II) Schiff base complexes is adapted from a literature procedure, and proceeds via the reaction scheme in Scheme 1, giving rise to complexes **1** (R = ethyl) and **2** (R = *iso*-propyl).⁵ These reactions can be performed on multi-gram scales using commercially available and inexpensive reagents.



Scheme 1. Preparation of Ni(II) Schiff base complexes.

The bis(salicylaldehyde) nickel(II) complex is easily prepared starting from salicylaldehyde and nickel(II) acetate tetrahydrate, and is isolated via simple filtration as a bright green powder. This is further reacted with the appropriate secondary amine by refluxing in ethanol to form the desired Schiff base complexes. The products are purified by recrystallization from chloroform and hexanes, giving rise to dark, well-formed crystals (Figure 1).



Figure 1. Ni(II) Schiff base complexes prepared in this work. From left to right: large crystals grown from a solution of **1** in chloroform and hexanes; recrystallized complex **1**; recrystallized complex **2**; isolated crystal of **1**, demonstrating the ease with which large crystals of these complexes can be grown and isolated.

RESULTS AND DISCUSSION

At first glance, nothing about these two solids suggests that they are very different; both complexes contain Ni(II) centers with virtually the same ligands, except for the functional group on nitrogen. They are both highly crystalline, dark green solids with comparable solubilities. However, their respective NMR data illustrates some key differences between the two. The ^1H and ^{13}C NMR spectra of **1** in CDCl_3 are shown in Figure 2. Both spectra contain the appropriate number of resonances, which are found in the expected regions. The resonance around 10 ppm in the ^1H spectrum is characteristic of the imine H, and this spectrum provides a good opportunity to learn about multiplicity, J -coupling and integrations.

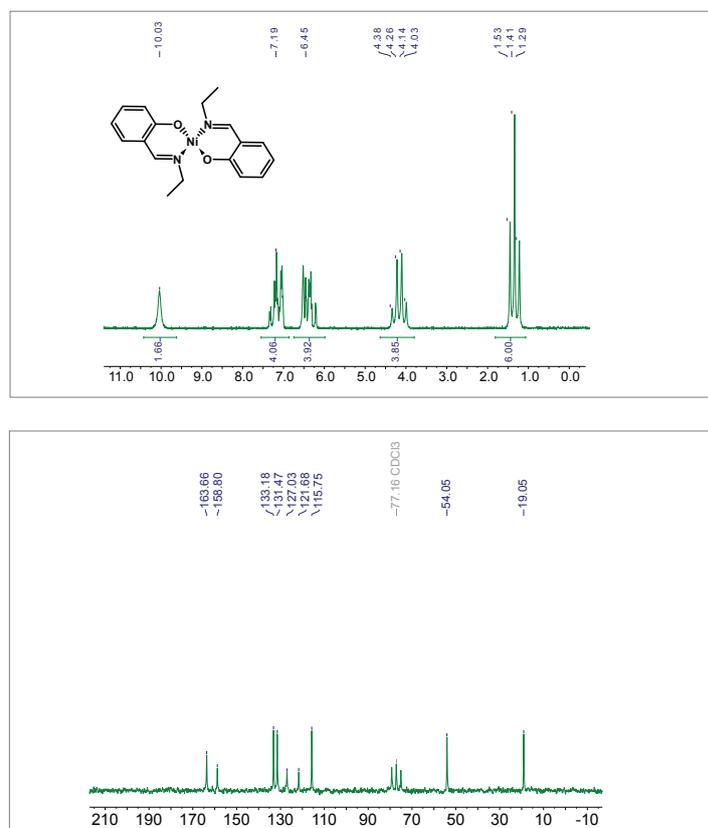


Figure 2. ^1H (top) and ^{13}C (bottom) NMR spectra of diamagnetic complex **1** in CDCl_3 .

While the spectra for complex **1** are relatively easy to elucidate, complex **2** requires more careful consideration. The ^1H and ^{13}C NMR spectra of **2** in CDCl_3 are shown in Figure 3. If the same spectral width of 12 ppm used to analyze complex **1** was selected for ^1H NMR, only 2 of the 7 expected signals would be observed. In fact, these 5 other signals are observed at -5.59 ppm, -5.32 ppm, 16.91 ppm, 93.83 ppm and 181.15 ppm, spanning approx. 185 ppm. With paramagnetic ^1H NMR, it can often be very difficult to assign resonances to the appropriate protons in the molecule. However, integrations can often still be reliable, and help with these assignments. Specifically, the signal at 5.76 ppm integrates to 12 protons, which can be assigned to the methyl groups. The extremely broad signal at 181.15 ppm can tentatively be assigned to the imine H, which would be significantly affected by the unpaired electrons on the metal due to proximity. Similarly, the C-H likely gives rise to the signal at 93.83 ppm. The remaining aromatic signals are very difficult to assign without additional experiments.

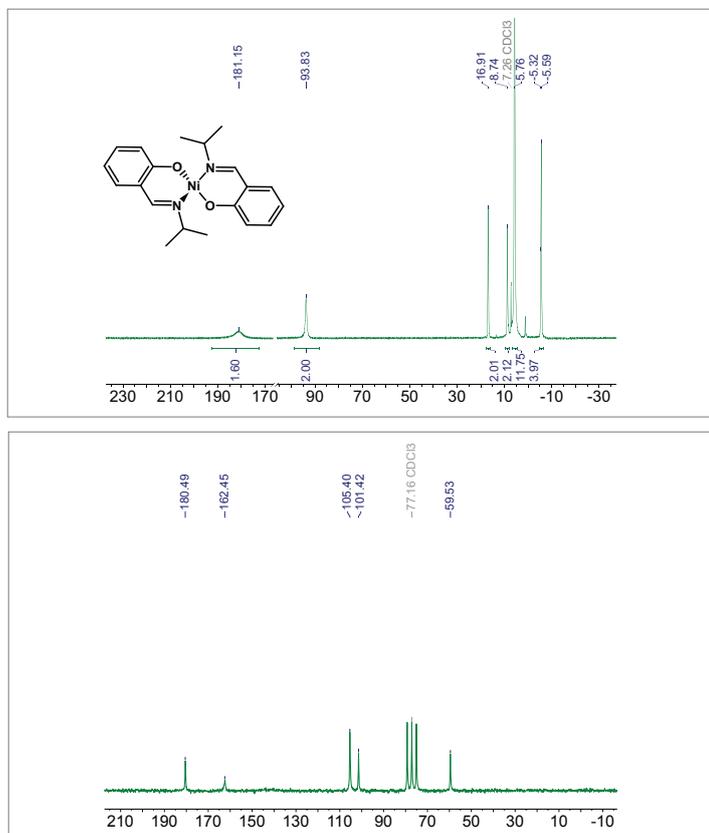


Figure 3. ^1H (top) and ^{13}C (bottom) NMR spectra of paramagnetic complex **2** in CDCl_3 .

Upon analysis of the ^{13}C NMR of complex **2**, only 5 of the 9 expected resonances could be observed. This is unfortunately a common reality for ^{13}C NMR of paramagnetic species, as the signals are often extremely broad, and a very large number of scans is often required to build up the necessary signal-to-noise ratio. This, coupled with the possibility that some signals might appear at typically very unlikely chemical shifts, makes it a challenge to observe all signals.

The origin of this paramagnetism can be explained based on the overall geometry of complexes **1** and **2**. Complex **1** is square planar, typical for Ni(II)/d^6 complexes. As such, the electrons populating the d-orbitals would all be paired ($n = 0$), and a diamagnetic complex is obtained ($S = 0$). Conversely, complex **2** is in fact tetrahedral, which is less common for Ni(II)/d^6 complexes. In this system, the electrons would populate the d-orbitals in such a way that 2 electrons are unpaired ($n = 2$), giving rise to a paramagnetic complex ($S = 1$). The respective d-orbital splitting of complexes **1** and **2** is shown in Figure 4.

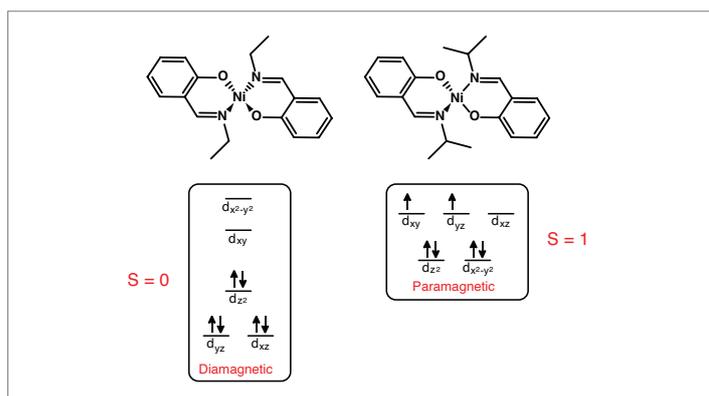


Figure 4. The d-orbital splitting for complexes **1** (left) and **2** (right), showing the distribution of electrons and origin of the diamagnetic vs paramagnetic behavior.

The differences in geometries between complexes **1** and **2** can likely be attributed to the size of the alkyl group on the imine nitrogen of the Schiff base ligand. While the CH_3 group within the ethyl fragment can be oriented away from the metal and the opposing oxygen atom, the $\text{CH}(\text{CH}_3)_2$ group of the fragment is unable to be oriented in the same way and occupies a larger, more spherical space around the metal and oxygen. As a result, the best solution to avoid these undesired steric interactions is a tetrahedral arrangement. Attempts to determine the effective magnetic moment of complex **2** by NMR using the Evans method⁶ were more difficult than initially anticipated, as these types of four-coordinate Ni(II) complexes are well-known to undergo a square planar-tetrahedral (diamagnetic-paramagnetic) conformational equilibrium in solution, which is both concentration and temperature dependent.⁷⁻⁹

CONCLUSION

The facile synthesis of two Ni(II) Schiff base complexes provides highly crystalline products, which are easy to isolate and amenable to analysis using ^1H and ^{13}C NMR. One of the complexes is diamagnetic and produces spectra consistent with its structure. However, the other is paramagnetic and gives rise to a ^1H spectrum with broad signals and extreme chemical shifts, as well as a ^{13}C spectrum with certain resonances that couldn't be observed. These experiments provide an excellent opportunity for students to learn about some of the experimentally observed effects of paramagnetism, as well as to gain a better understanding of how different functional groups can alter the geometry and distribution of electrons within the d-orbitals of a transition metal complex.

References

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“Purchasing an instrument is often a complex interplay of multiple criteria, including cost, quality, ease of use, and maintenance. For Southwestern College, the 60e was the perfect match for our criteria, and we have no regrets about our choice.”

— Dr. Michael Tessmer, Professor,
Southwestern College